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(72) Inventors:
• Denis Guesquiere
27370 Tourville la Campagne (FR)
• Daniel Loc'h
76570 Mesnil Panneville (FR)

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(71) Applicant: WITCO
75008 Paris (FR)

(74) Attorney:
Jacques Peuscet
Cabinet Peuscet
78, avenue Raymond Poincaré
75116 Paris (FR)

(54) Polyurethane molding process using an internal mold releasing agent and the obtained molded products

(57) Polyurethane molding process according to which one introduces into a mold a mixture containing at least one isocyanate prepolymer and at least one hydroxylated organic compound capable of reacting with said prepolymer, an internal mold releasing agent being added to said mixture, in which said internal mold releasing agent is composed of at least one diester of at least one aliphatic, aromatic, alicyclic or dimeric diacid and of at least one linear or branched aliphatic monohydric alcohol, said diester having a total of 24 to 52 carbon atoms.

[0001] The current invention concerns a polyurethane molding process, in which one uses an internal mold releasing agent, as well as the molded products obtained from this process, in particular, shoes comprising a molded sole.

[0002] It is a known polyurethane molding process to introduce into an open or closed mold a mixture containing an isocyanate prepolymer and at least one hydroxylated compound, in particular a polyether polyol or a polyester polyol having a functionality being at least equal to 2, capable of reacting with the isocyanate prepolymer, as well as various additives such as expansion agents, catalysts, stabilizers and reinforcing fillers or agents.

[0003] It is a known process to spray on molds, prior to their use, an external mold releasing agent, such as a wax or silicone, generally in the form of a solution in a solvent or in the form of an aqueous dispersion. In the absence of an internal mold releasing agent, it is necessary to effect a second spraying step on the surface of the mold after each release of the mold.

[0004] It is a known process, furthermore, to add an internal mold releasing agent in with the mixture to be molded, the purpose of which allows repeated mold release use before it is required to once again reapply an external mold releasing spray agent. The higher the number of mold releases, the more the molding rate can be increased, and as a result, the more economical the process will be. Besides, a quantitative reduction in the amount of external mold releasing agent used also entails a reduction in the cost of manufacturing and leads to an improvement on the ecological plane due to the decrease in the quantity of evaporated solvent released into the atmosphere as well as a decrease in the quantity of external mold releasing agent sprayed beyond the mold.

[0005] It is a known process also, for example from US patent 5,389,696, to introduce into a mixture to be molded, an internal mold releasing agent, at a rate of 1 to 10 weight percent relative to the total weight of the mixture to be molded, which contains mixed esters containing 1) diacids, 2) polyols and 3) carboxylic monoacids with 12 to 30 carbon atoms. It is expressly indicated, in lines 35 - 38 of column 2, that this agent must not contain any esters of diacids or any aliphatic monohydric alcohols having 12 to 30 carbon atoms. When such an agent is used, it is difficult to dose because it does not mix well with the prepolymer and/or with the polyol.

[0006] According to the present invention, it has been found that certain diesters can be used alone as internal mold releasing agents with results that are better than the results obtained from the mixture advocated by US patent 5,389,696 from which patent they are explicitly excluded.

[0007] Therefore, the object of the present invention is a polyurethane molding process according to which one introduces into a mold a mixture containing at least one isocyanate prepolymer and at least one hydroxylated organic compound capable of reacting with said prepolymer, an internal mold releasing agent being added to said mixture, characterized by the fact that said internal mold releasing agent is composed of at least one diester of at least one aliphatic, aromatic, alicyclic or dimeric diacid, and of at least one linear or branched aliphatic monohydric alcohol, said diester comprising a total of 24 to 52 carbon atoms, but preferably 26 to 36 carbon atoms. By preference, a diester of a monohydric alcohol is used comprising a number of carbon atoms ranging between 7 and 14.

[0008] The diesters used can be, for example, diisodecyl phthalate, diisoundecyl phthalate, diisotridecyl phthalate, diisononyl adipate, diisodecyl adipate, diisotridecyl adipate, di-n (C12 - C 14)- alkyl adipate, 2- ethyl hexyl dodecanedioate, n-octyl dodecanedioate, the ester

of an oleic acid dimer and of 2- ethyl hexyl alcohol (2- ethyl hexyl dimerate), and the ester of an oleic acid dimer and of n-octyl alcohol (n- octyl dimerate), these diesters allowing products to be molded all in one piece, in particular in the form of one single layer in density.

[0009] Used by preference are diisotridecyl phthalate, diisotridecyl adipate, di-n (C12 - C 14)-alkyl adipate, 2- ethyl hexyl dodecanedioate, n-octyl dodecanedioate, 2- ethyl hexyl dimerate and n- octyl dimerate which simultaneously allow for manufacturing molded products that are all in one piece with one single density as well as some molded products in the form of two different coupled parts, specifically with possibly differing density layers adhering to one another. In an especially preferred manner, one uses diisotridecyl phthalate, diisotridecyl adipate, n-octyl dodecanedioate and n- octyl dimerate, being that diisotridecyl phthalate and diisotridecyl adipate are particularly preferred.

[0010] It has been found that these diesters, defined in the active proportions hereinafter, easily mix well enough with the isocyanate prepolymer and/or with the hydroxylated compound capable of reacting with the prepolymer so that it is possible to introduce them into the mold as a mixture with the prepolymer, as a mixture with the hydroxylated compound/s capable of reacting with the prepolymer, or as a mixture with both of them. Furthermore, the diesters in accordance with the invention can be independently introduced into the mixing head of the molding machines at the same time as the other compounds of the mixture. This mode of introduction is especially favorable in the case where the diester is a dimerate.

[0011] The diesters according to the invention specifically allow molding polyurethanes having a density ranging between 0.2 and 1.25 g/cm³, a density namely obtained by varying the weight percentage of the expansion agent in the total mixture.

[0012] The quantity of diesters that is added ranges between 1 and 5% in weight relative to the total weight of the molding mixture. If quantities of less than 1% are used, the number of moldings that can be effected after using an external mold releasing agent is not increased. If quantities greater than 5% are used, there is no significant increase in the number of moldings effected in between any two consecutive applications of external mold releasing agent. The external mold releasing agent that is preferably used is a mixture of linear and/or cyclic polydimethyl siloxanes and/or of polydimethyl siloxanes with hydroxyl terminations with which the mold is coated initially and then again after a certain number of consecutive molding cycles without coating.

[0013] The isocyanate prepolymer can be obtained from any known isocyanate used in the preparation of polyurethanes, whether they be aliphatic, cycloaliphatic, aryl, aryl aliphatic or heterocyclic. One uses, for example, methylene diphenyl isocyanate.

[0014] The hydroxylated compound can be a polyether polyol or a polyester polyol. According to the invention, one uses, by preference, a polyester polyol, in particular a polyadipate. It can also contain polyols with a molecular weights of less than 400 in the sense that they are chain elongators.

[0015] The mixture to be molded can contain, in a known manner, other additives besides the internal mold releasing agent. One can cite expanding agents such as water, halogenated hydrocarbons, solvents with low boiling points such as pentane, catalysts such as tertiary amines, emulsifiers or foam stabilizing agents such as siloxanes, mineral and organic fillers such as glass fibers, mica, talcum, calcium carbonate or organic microballoons such as those sold by the

NOBEL INDUSTRIES Corporation under the brand name of "EXPANDOCEL". One can also include additives such as flame retarding agents, antistatic agents, coloring agents and cellular regulators. One must note that no liquid diluting agents are added in general such as mineral oil, vegetable oil or cyclic olefin.

[0016] The use of an internal mold releasing agent in accordance with the invention is specifically adapted to the molding of microcellular soles for shoes, namely of closed cell soles. The soles can be manufactured separately and then affixed by adhesion on to the shank of the shoe or they can be molded by injection directly on to the shank of the shoe. In this case, we have found that the use of diesters in accordance with the invention ensures in maintaining good adhesion of the polyurethane sole to the shank, in particular to a shank made of leather.

[0017] According to the present invention, one can also prepare so-called "coupled" soles comprised of two layers: one wear layer that is relatively compact with a density of about 1 to 1.25 and a comfort layer having a lower density of about 0.4. In this case, the shank can also be directly joined with the sole during the molding process. We have confirmed that the two layers adhere properly to one another and that the low density layer adheres to the shoe shank when there is direct injection on to the said shank.

[0018] The use of diesters according to the invention makes it possible to effect at least 10 molding cycles and up to more than 50 consecutive molding cycles before it is necessary to reapply an external mold releasing agent on the surface of the mold. Therefore, mold use frequency can be very markedly improved and, as a result, production time and costs can be lowered as well, and so can pollution due to the evaporation of the solvent in the external mold releasing agent as well as the quantity of external mold releasing agent sprayed beyond the mold. The addition of diesters according to the invention does not modify the reaction: manufacturing can be done at the same temperatures with the same product ratios as previously without their use.

[0019] The invention also has the object of producing a molded product, and namely a sole of a shoe, that is obtained by application of the above defined process as well as a shoe whose sole is thus obtained.

[0020] The assays provided below, for the purpose of providing examples on a purely illustrative and non-restrictive basis, shall allow for a better understanding of the invention.

General molding method

[0021] The assays have been conducted on two machines:

- 1) a commercial machine by the "GUSBI" Corporation, with which casting of the mixture to be molded is effected into an open mold,
- 2) a commercial machine by the "DESMA" Corporation with which the mixture to be molded is injected into a closed mold.

[0022] The molds used are made of an aluminum alloy. Prior to any assay, they are carefully cleaned with N-methyl pyrrolidone, then rinsed with methylene chloride and dried in the open air.

They are heated at 40 - 45°C.

[0023] An external mold releasing agent (refer to table V) is applied to the molds with a spray gun prior to the first molding cycle. No other spraying application is done so long as it is possible to obtain soles or plates that do not stick, that are free of defects and more generally, so long as no particular intervention is called for.

[0024] The molds used are strictly of the same type as those used industrially in the manufacturing of either one piece soles (single mold) intended to be adhered on to the shank of the shoe, or of soles with a single density injected directly over the shank, or of "coupled" type soles composed of one wear layer with a higher density and of one comfort layer with a lower density that are injected in sequence. The plate molds have the following dimensions: 15 X 20 cm and vary in thickness from 0.5 to 1 cm.

[0025] In all cases, the time periods for mold releasing or mold opening have been maintained at their standard values, that is to say at the value used when there is no internal mold releasing agent used. Depending on the polyurethane under preparation and on the type of mold used, these time periods vary between 1.5 and 3 minutes.

Products used for molding

[0026] They are obtained by reacting a prepolymer of methylene diphenyl isocyanate (MDI) with a polyol composition including a polyester polyol that is a polyadipate.

Polyadipates

[0027] Three types of polyadipates have been used which differ by the polyols used or by their molecular weight.

TABLE I

Polyadipate	Polyols used	Molecular weight
Polyadipate I	ethylene glycol 60% diethylene glycol 40%	2,000
Polyadipate II	ethylene glycol 70% butane diol 30%	2,000
Polyadipate III	ethylene glycol 70% butane diol 30%	3,000

Internal mold releasing agents

[0028] The internal mold releasing agents used are provided in table II below.

TABLE II

DIESTER	total number of carbons	DEx reference
diisodecyl phthalate	28	DE1
diisoundecyl phthalate	30	DE2
diisotridecyl phthalate	34	DE3
diisononyl adipate	24	DE4
diisodecyl adipate	26	DE5
diisotridecyl adipate	32	DE6

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di- n- alkyl C12 - C14 adipate (1)	≈ 31.6	DE7
2-ethyl hexyl dodecanedioate	28	DE8
n- octyl dodecanedioate	28	DE9
2- ethyl hexyl dimerate (2)	52	DE10
n- octyl dimerate (2)	52	DE11

- (1) Obtained based on the mixture of alcohols C12/C14 = 70/30 "NAFOL" 12 - 14 S by Condea Corp.
(2) Obtained with dimer acids "PRIPOL 1017" by Unichema Corp.

Prepolymers

[0029] Three types of prepolymers (A, B and C) have been prepared with 16.5% NCO relative to the DEx diester in question.

TABLE III

Composition of the prepolymers	Reference
MDI + polyadipate I	A
MDI + polyadipate + 4% diester DEx	BDEx
MDI + polyadipate + 7% diester DEx	CDEx

Composition of the polyols

[0030] One mixes a polyadipate, that is a polyester polyol, with different additives in such a manner as to obtain the compositions provided in table IV.

TABLE IV

Reference	Composition of the polyols	Weight %
1	polyadipate II ethylene glycol (chain elongator) triethylene diamine (catalyst)	95.40 3.60 1.00
2 DEx	same as 1 + 2% diester DEx	
3 DEx	same as 1 + 4% diester DEx	
4	polyadipate II ethylene glycol (chain elongator) triethylene diamine (catalyst) NIAX silicone SR 393* (cell stabilizer) water (expanding agent)	88.55 10.30 0.40 0.40 0.35
5 DEx	same as 4 + 2% diester DEx	

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6	polyadipate III ethylene glycol (chain elongator) triethylene diamine (catalyst) NIAX silicone SR 393* (cell stabilizer) water (expanding agent)	89.45 9.00 0.70 0.40 0.45
7 DEx	same as 6 + 2% diester DEx	
8	polyadipate II ethylene glycol (chain elongator) triethylene diamine (catalyst) NIAX silicone SR 393* (cell stabilizer) water (expanding agent)	89.95 8.50 0.60 0.40 0.55
9 DEx	same as 8 + 2% diester DEx	
10 DEx	same as 8 + 4% diester DEx	

*NIAX silicone SR 393 = silicone surface active agent commercialized by "WITCO Corporation"

TABLE IV (continued)

Reference	Composition of the polyols	Weight %
11	polyadipate II ethylene glycol (chain elongator) triethylene diamine (catalyst)	93.40 5.60 1.00
12 DEx	same as 11 + 2% DEx	

[0031] We introduced a prepolymer defined above in table III and a composition of polyols defined above in table IV into the molds in the weight proportions (prepolymer/ composition of polyols) indicated in table V under the letter "R". The constituents are heated at 45 - 50°C. We counted the number of molding cycles after the initial spraying of an external mold releasing agent up to the point when a second spraying was required, and eventually after a second spraying, when a third spraying was required. The assays were effected with a "GUSBI" casting machine or with a "DESMA" injection machine. In the case of molding layers of single density (one piece moldings), the results are provided in table V hereafter; in this table, the first two rows of assays correspond to plate moldings while the other remaining rows correspond to shoe sole moldings.

TABLE V

ONE PIECE MOLDINGS								
Density	Machine	Polyol	Prepolymer	R	Diester % in mix	External mold releasing agent	Initial number of molding cycles	Cycle number after 2 nd spraying
1.2	Gusbi	1	A	0.54	0.0	AP 7014-89 (1)	3 - 5	-
1.2	Gusbi	3 DE6	A	0.53	2.6	AP 7014-89	40 - 45	40 - 45

1.2	Desma	1	A	0.53	0.0	AP 7014-89	3 - 5	-
1.2	Desma	3 DE6	A	0.52	2.6	AP 7014-89	> 30*	-
1.2	Desma	1	BDE6	0.54	1.4	AP 7014-89	20 - 25	20 - 25
1.2	Desma	1	CDE6	0.54	2.5	AP 7014-89	> 30*	-
1.2	Desma	12 DE1	BDE1	0.68	2.8	FZ 3711 (2)	10 - 12	-
1.2	Desma	11	A	0.70	0.0	FZ 3711	4 - 6	-
1.2	Desma	12 DE2	BDE2	0.69	2.8	FZ 3711	10 - 11	-
1.2	Desma	12 DE3	BDE3	0.68	2.8	FZ 3711	> 30*	-
1.2	Desma	2 DE4	BDE4	0.53	2.7	AP 7014-89	10 - 12	-

1.2	Desma	2 DES	BDE5	0.52	2.7	AP 7014-89	10 - 11	-
1.2	Desma	12 DE5	BDE5	0.68	2.8	FZ 3711	12 - 13	-

*assay stopped before reaching the system limit

(1) Mold releasing agent by Air Products Corporation

(2) Silicone fluid FZ 3711 by Witco Corporation

TABLE V (continued)

ONE PIECE MOLDINGS								
Density	Machine	Polyol	Prepolymer	R	Diester % in mix	External mold releasing agent	Initial number of molding cycles	Cycle number after 2 nd spraying
1.2	Desma	3 DE5	BDE5	0.53	4.0	AP 7014-89	10 - 12	-
1.2	Desma	12 DE6	BDE6	0.68	2.8	FZ 3711	55	50
1.2	Desma	12 DE6	BDE6	0.68	2.8	Siliconol NM1-100 (3)	> 25*	-
1.2	Desma	12 DE7	BDE7	0.68	2.8	FZ 3711	> 30*	-
1.2	Desma	12 DE8	BDE8	0.68	2.8	FZ 3711	> 40*	-
1.2	Desma	12 DE9	BDE9	0.68	2.8	FZ 3711	24 - 25	-
1.2	Desma	2 DE10	BDE10	0.54	2.7	AP 7014-89	27 - 28	-
1.2	Desma	12DE11	BDE11	0.69	2.8	FZ 3711	12 - 14	-
0.55	Gusbi	4	A	1.17	0.0	AP 7014-89	2 - 3	-
0.55	Gusbi	4	BDE6	1.17	2.2	AP 7014-89	10 - 12	-
0.55	Gusbi	5 DE6	BDE6	1.17	3.1	AP 7014-89	15 - 20	-
0.55	Desma	6	A	1.02	0.0	AP 7014-89	3 - 4	-
0.55	Desma	6	CDE6	1.02	3.5	AP 7014-89	15 - 20	-
0.55	Desma	7 DE6	BDE6	1.02	3.0	AP 7014-89	15 - 20	-
0.45	Desma	8	A	1.08	0.0	AP 7014-89	2 - 3	-
0.45	Desma	8	BDE6	1.08	2.1	AP 7014-89	25 - 30	25 - 30
0.45	Desma	8	CDE6	1.08	3.6	AP 7014-89	> 30*	-

*assay stopped before reaching the system limit

(3) Silicone oil: polydimethyl siloxane by Hüls Corporation

[0032] The polyurethanes having a density of 1.2 correspond to the wear layers of the "coupled" soles, the polyurethanes having a density of 0.45 correspond to the comfort layers of the "coupled" soles and the polyurethanes with a density of 0.55 correspond to mono-layer soles (monodensity).

[0033] These assays demonstrate that in the presence of diesters according to the invention, the number of molding cycles possible markedly increases in between two consecutive external mold releasing agent spraying operations.

[0034] We also effected molding assays for two layers of different density by sequential injections ("coupled" soles), the first layer corresponding to a wear layer having a density of 1.2 and the second layer corresponding to a comfort layer having a density of 0.45. We used a "DESMa" injection machine. The results are provided in table VI.

TABLE VI
COUPLED SOLES

COUPLED SOLES										
Wear layer (d = 1.2)				Comfort layer (d = 0.45)				External mold releasing agent	Number of molding cycles (1)	
Polyol	Prepolymer	R	Diester %	Polyol	Prepolymer	R	Diester %		after 1 st spraying	after 2 nd spraying
1	A	0.54	0.0	8	A	1.08	0.0	AP 7014-89 (2)	3 - 5	-
3 DE6	A	0.53	2.6	10 DE6	A	1.08	1.9	AP 7014-89	50	45 - 50

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2 DE6	BDE6	0.53	2.7	8	BDE6	1.08	2.1	AP 7014-89	30 - 35	30 - 35
2 DE6	BDE6	0.53	2.7	9 DE6	BDE6	1.06	3.0	AP 7014-89	> 35 (*)	-
12 DE3	BDE3	0.68	2.8	9 DE3	BDE3	1.06	3.0	FZ 3711 (3)	56	45 - 50
11	CDE6	0.69	2.9	8	CDE6	1.08	3.6	FZ 3711	62	-
12 DE9	BDE9	0.68	2.8	9 DE9	BDE9	1.06	3.0	FZ 3711	> 25 (*)	-

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12 DE11	BDE11	0.68	2.8	9 DE11	BDE11	1.06	3.0	FZ 3711	13 - 16	-
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(*) Stopped before reaching the possible limit

(1) number of molding cycles possible without defect on the two layers, either one being acceptable.

(2) AP 7014-89: mold releasing agent by Air Products Corporation.

(3) Silicone fluid FZ 3711 by Wilco Corporation.

[0035] In this case as well we see that in the presence of diesters in accordance with the invention, that the number of mold releases possible markedly increases in between two consecutive external mold releasing agent spraying operations.

[0036] We measured as per norm EN 344 (paragraph 5.1) the adherence between the two layers, which ranges from 4.2 to 7.5 N/mm, on the coupled moldings corresponding to the fourth row in table VI and the adherence between the comfort layer and a leather shank, which ranges from 6 to 10 N/mm. These adherence values are appropriate, since, for example, the minimum adherence value must be 4 N/mm according to norm EN 344 .

Claims

1. Polyurethane molding process according to which one introduces into a mold a mixture containing at least one isocyanate prepolymer and at least one hydroxylated organic compound capable of reacting with said prepolymer, an internal mold releasing agent being added to said mixture, characterized by the fact that said internal mold releasing agent is composed of at least one diester of at least one aliphatic, aromatic, alicyclic or dimeric diacid, and of at least one linear or branched aliphatic monohydric alcohol, said diester comprising a total of 24 to 52 carbon atoms.
2. Molding process according to claim 1, characterized by the fact that the diester or the weighted mixture of diesters comprises a total of 26 to 36 carbon atoms.
3. Molding process according to one of the claims 1 or 2, characterized by the fact that the monohydric alcohol comprises 7 to 14 carbon atoms.
4. Molding process according to one of the claims 1 through 3, characterized by the fact that the diester is diisotridecyl phthalate or diisotridecyl adipate.
5. Molding process according to one of the claims 1 through 4, characterized by the fact that the diester is introduced into the mold as a mixture with the prepolymer, with the hydroxylated organic compound/s or with both of the two constituents.
6. Molding process according to one of the claims 1 through 4, characterized by the fact that the diester is introduced independently into the mixing head of a molding machine comprising the mold.
7. Molding process according to one of the claims 1 through 6, characterized by the fact that the quantity of diester introduced is included between 1 and 5% in weight relative to the total weight of the molding mixture.
8. Molding process according to one of the claims 1 through 7, characterized by the fact that

the hydroxylated organic compound is a polyester polyol having a functionality of at least 2.

9. Molding process according to claim 8, characterized by the fact that the polyester polyol is a polyadipate.
10. Molding process according to one of the claims 1 through 9, characterized by the fact that initially and after a certain number of consecutive molding cycles, the mold is coated with an external mold releasing agent comprising one or several linear and/or cyclic polydimethyl siloxane/s and one or several polydimethyl siloxane/s with hydroxyl terminations.
11. Molding process according to one of the claims 1 through 10, characterized by the fact that microcellular soles are molded for shoes.
12. Molding process according to one of the claims 1 through 11, characterized by the fact that soles are molded comprising two layers of different density.
13. Molded product obtained by the application of the process according to one of the claims 1 through 12.
14. Shoe comprising a sole molded by the application of the process according to one of the claims 1 through 12.